

*Electronic Supplementary Information (ESI) for B921451H*

# Creation of highly efficient solid emitter by decorating pyrene core with AIE-active tetraphenylethene peripheries

*Zujin Zhao, Shuming Chen, Jacky W. Y. Lam, Ping Lu, Yongchun Zhong, Kam Sing Wong, Hoi Sing Kwok  
and Ben Zhong Tang\**

## Table of Contents

<b>Experimental Section</b>	(S2)
<b>Figure S1.</b> MALDI-TOF mass spectrum of TTPEPy.	(S5)
<b>Figure S2.</b> XRD diffractogram of as-prepared powder of TTPEPy.	(S5)
<b>Figure S3.</b> UV and PL spectra of TTPEPy in THF solutions with different concentrations.	(S6)
<b>Figure S4.</b> PL spectra of TTPEPy in THF solution (1 $\mu$ M) at 298 and 77 K.	(S6)
<b>Figure S5.</b> PL decay curves of a) THF solution (1 $\mu$ M) and b) crystalline powder of TTPEPy at different temperatures.	(S7)
<b>Figure S6.</b> PL spectra of the powder and film of TTPEPy at 298 and 77 K.	(S7)

## Experimental Section

**General Information.** THF was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. All other chemicals and reagents were purchased from Aldrich and used as received. 1-(4-Bromophenyl)-1,2,2-triphenylethylene (**1**)<sup>1</sup> and 1,3,6,8-tetrabromopyrene<sup>2</sup> were prepared according to previously published procedures.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker AV 300 spectrometer in deuterated chloroform using tetramethylsilane (TMS;  $\delta = 0$ ) as internal reference. UV spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. PL spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. MALDI-TOF mass spectrum was recorded on a GCT premier CAB048 mass spectrometer. Cyclic voltammetry curves were taken on a Princeton Applied Research (model 273A) potentiostat. All the measurements were carried out at room temperature using a conventional three-electrode configuration in distilled dichloromethane with Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) as supporting electrolyte. The working and reference electrodes were glassy carbon and Ag/AgNO<sub>3</sub> (0.1 M in acetonitrile), respectively. The reference electrode was checked vs. ferrocene as recommended by IUPAC. All solutions were deaerated by bubbling nitrogen gas for a few minutes prior to measurements. Elemental analysis was performed on an Elementary Vario EL analyzer. Thermogravimetric analysis was carried on a TA TGA Q5000 under nitrogen at a heating rate of 10 °C/min. Thermal transitions were studied with differential scanning calorimetry using a TA DSC Q1000 under nitrogen at a heating rate of 10 °C/min. X-ray diffraction diagram was recorded on a Philips PW 1830 powder diffractometer using the monochromatized X-ray beam from a nickel-filtered Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ).

**Device Fabrication.** OLED devices were fabricated on 80 nm ITO coated glass with a sheet resistance of 25 $\Omega/\square$ . Prior to loading into the pretreatment chamber, the ITO-coated glasses were soaked

in ultrasonic detergent for 30 min, followed by spraying with de-ionized water for 10 min, soaking in ultrasonic de-ionized water for 30 min, and oven-baking for 1 h. The cleaned glasses were treated by perfluoromethane (CF<sub>4</sub>) plasma with a power of 100 W, a gas flow of 50 sccm, and a pressure of 0.2 Torr for 10 s in the pretreatment chamber. The glasses were transferred to the organic chamber with a base pressure of  $7 \times 10^{-7}$  Torr for depositions of *N,N*-bis(1-naphthyl)-*N,N*-diphenylbenzidine (NPB), TTPEPy, and 2,2',2''-(1,3,5-benzinetriyl)tris(1-phenyl-1-H-benzimidazole) (TPBi), which respectively served as hole-transporting, light-emitting, and electron-transporting layers. The samples were then transferred to the metal chamber for cathode deposition which is lithium fluoride (LiF) capped with aluminum (Al).

The light-emitting area of the OLED was 4 mm<sup>2</sup>. The current density–voltage characteristics of the devices were measured by a HP4145B semiconductor parameter analyzer. The forward direction photons emitted from the devices were detected by a calibrated UDT PIN-25D silicon photodiode. The luminance and external quantum efficiencies of the devices were inferred from the photocurrent of the photodiode. The electroluminescence spectra were obtained on a PR650 spectrophotometer. All the measurements were carried out under air at room temperature without device encapsulation.

**Preparation of Luminogen Nanoaggregates.** Stock THF solution of TTPEPy with a concentration of 10 μM was prepared. Aliquots of the stock solution were transferred to 10 mL volumetric flasks. After appropriate amounts of THF were added, water was added dropwise under vigorous stirring to furnish 1 μM solutions with different water fractions ( $f_w = 0\text{--}99.5$  vol %). PL spectra of the resultant nanoaggregate suspensions were measured immediately after the sample preparation.

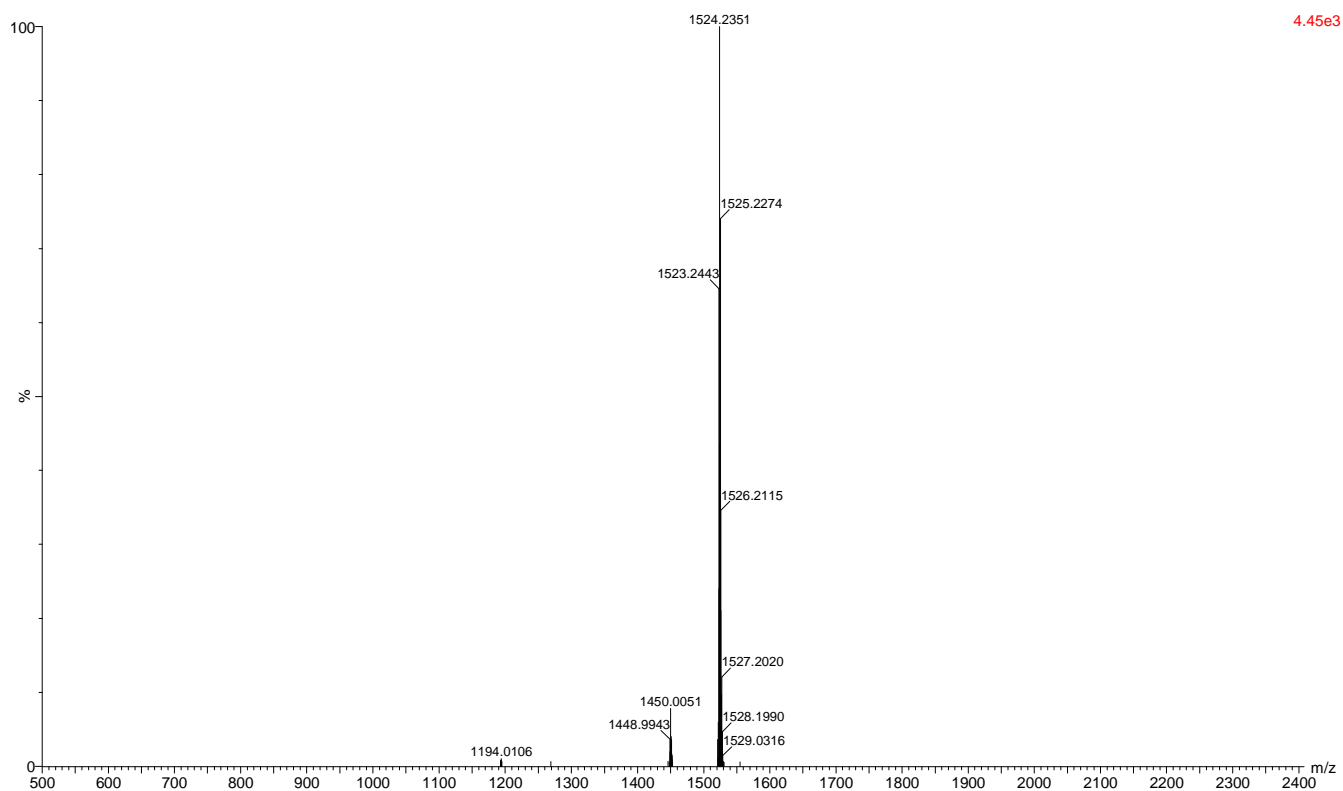
**Synthesis of 4-(1,2,2-Triphenylvinyl)phenylboronic acid (2).** Into a 250 mL two-necked round-bottom flask under nitrogen was slowly added *n*-butyllithium (1.6 M in hexane, 7.5 mL, 12 mmol) and a THF solution (80 mL) of **1** (4.11 g, 10 mmol) at  $-78$  °C. After stirring for 3 h, 2.4 mL of trimethyl

borate (20 mmol) was added into the reaction mixture. The mixture was warmed to room temperature and the reaction was terminated by adding hydrochloric acid (2 M, 10 mL) after 12 h. The mixture was then poured into water and extracted with dichloromethane. The organic layer was washed by water and dried over magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate as eluent. White solid of **2** was obtained in 70% yield (2.6 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ(TMS, ppm): 7.88 (d, 2H, *J* = 8.1 Hz), 7.13–7.00 (m, 17H), 4.49 (s, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>), δ(TMS, ppm): 148.9, 144.2, 144.1, 144.09, 142.4, 141.4, 135.6, 133.5, 132.0, 131.6, 128.4, 128.3, 127.4, 127.2. MS (MALDI-TOF): *m/z* 376.2030 (M<sup>+</sup>, calcd 376.1635).

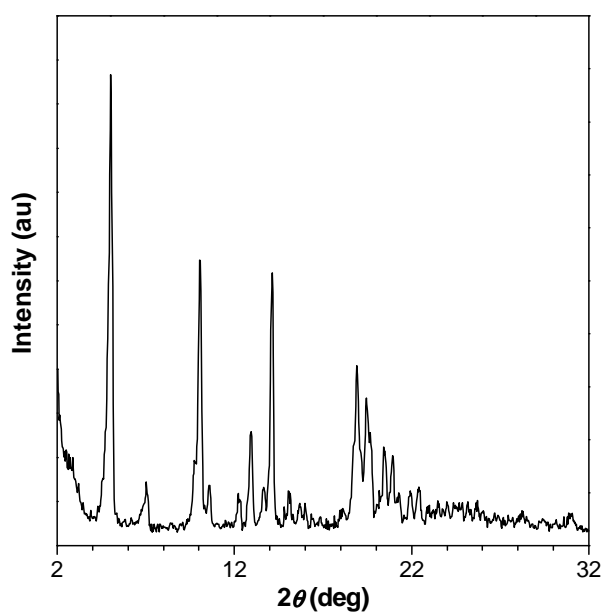
**Synthesis of 1,3,6,8-Tetrakis[4-(1,2,2-triphenylvinyl)phenyl]pyrene (TTPEPy).** A solution of **2** (2.3 g, 6 mmol), 1,3,6,8-tetrabromopyrene (0.52 g, 1 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (200 mg, 0.2 mmol), and potassium carbonate (2.8 g, 20 mmol) in 120 mL of a degassed toluene/ethanol/water mixture (8:2:2 v/v/v) was heated to reflux for 24 h under nitrogen. The precipitate was filtrated and washed with water, acetone and THF. After drying under vacuum, the product was purified by sublimation under vacuum. A pale green solid was obtained in 50% yield (0.76 g). The product was partially soluble in toluene and benzene. No NMR spectra were measured because of its limited solubility in organic solvents. MS (MALDI-TOF): *m/z* 1524.2351 [(M+H)<sup>+</sup>, calcd 1524.6450]. Anal. Calcd for C<sub>120</sub>H<sub>82</sub>: C, 94.58; H, 5.42. Found: C, 94.29; H, 5.70.

## References

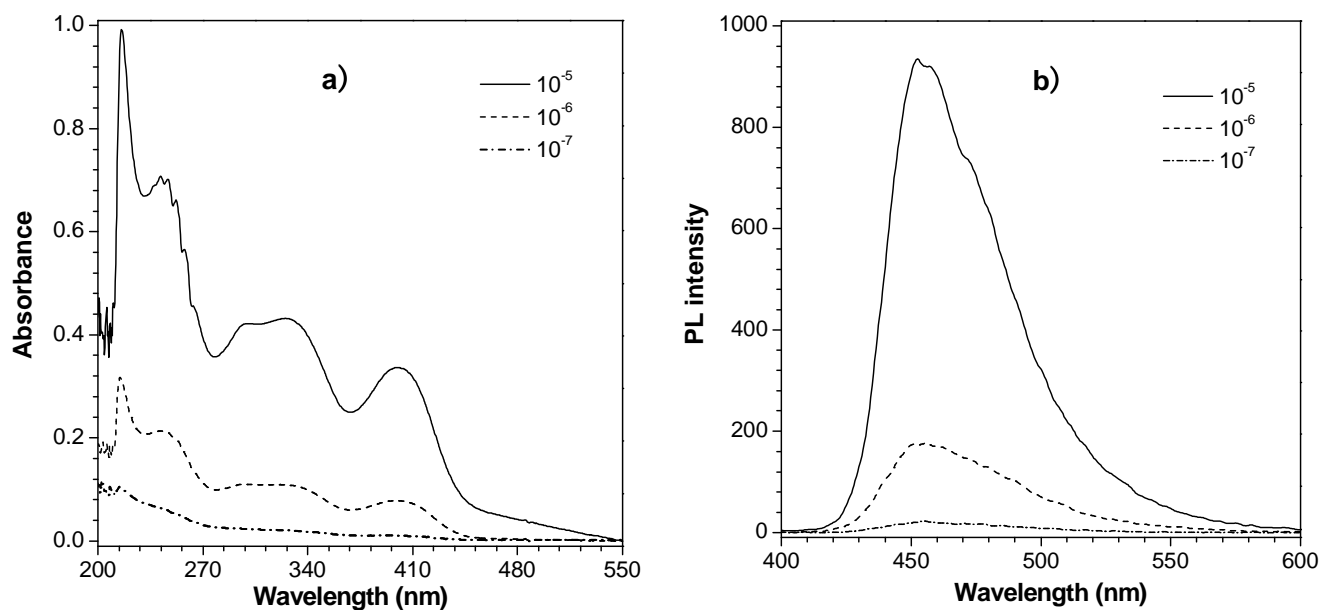
- (1) M. Banerjee, S. J. Emond, S. V. Lindeman and R. Rathore, *J. Org. Chem.*, 2007, **72**, 8054.
- (2) G. Venkataramana and S. Sankararaman, *Eur. J. Org. Chem.*, 2005, 4162.



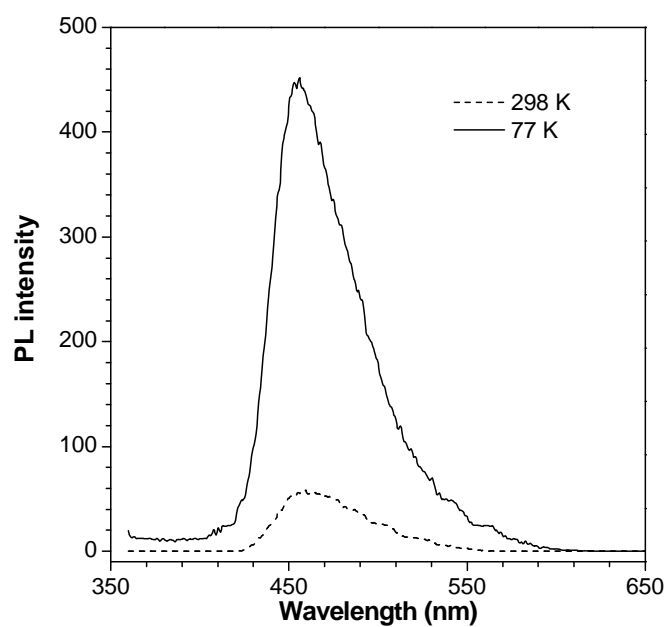
**Figure S1.** MALDI-TOF mass spectrum of TTPEPy.



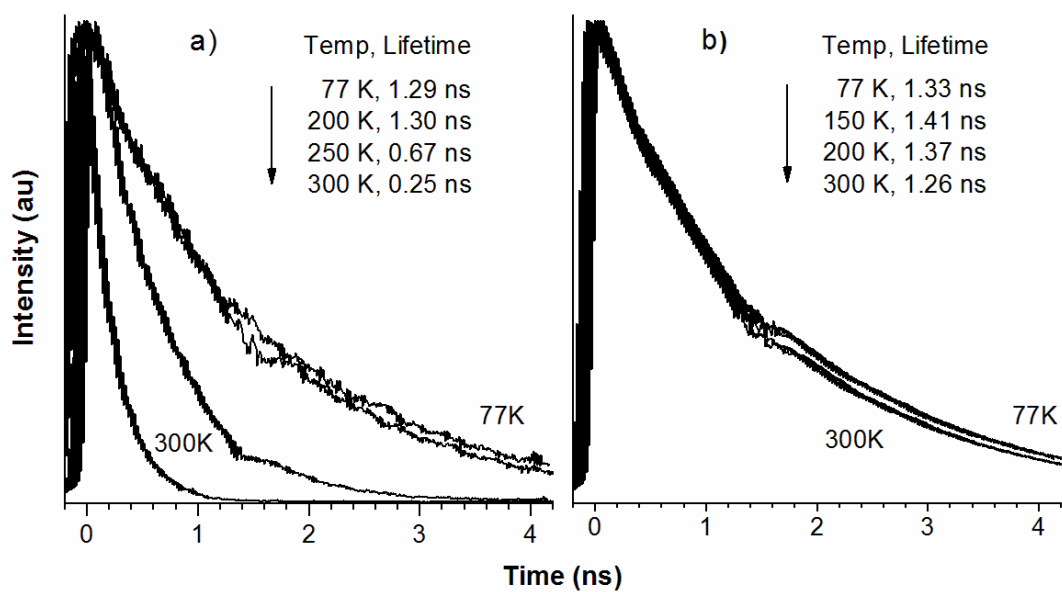
**Figure S2.** XRD diffractogram of as-prepared powder of TTPEPy.



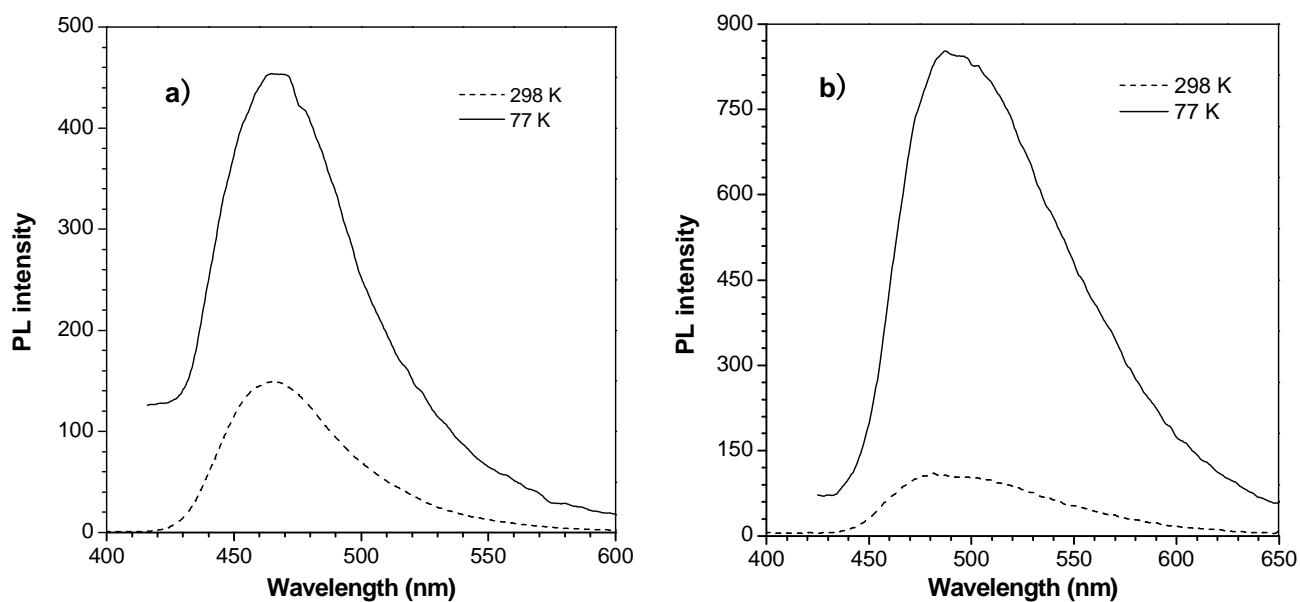
**Figure S3.** UV and PL spectra of TTPEPy in THF solutions with different concentrations.



**Figure S4.** PL spectra of TTPEPy in THF solution (1  $\mu$ M) at 298 and 77 K.



**Figure S5.** PL decay curves of a) THF solution (1  $\mu$ M) and b) crystalline powder of TTPEPy at different temperatures.



**Figure S6.** PL spectra of the powder and film of TTPEPy at 298 and 77 K.